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Pb(II) Adsorption by a Calcium Metal-Organic Framework †

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Abstract: Among the water pollution sources, heavy metals are considered the most hazardous because of their high toxicity to human health and their ability to badly damage the kidneys, brain, and nerves, as well as cause birth defects. Based on the promising features of metal-organic frameworks (MOFs), they could act as a favorable candidate in heavy metal removal applications. A calcium-based metal-organic framework was synthesized by the deposition method using benzene-1,2,4,5-tetracarboxylate as a linker. After characterization of the MOF was performed using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) analyses, it was applied to efficient adsorption of Pb(II) pollutant ions. The potential of obtained MOF, $[Ca(H_2btec)\cdot H_2O]_n$, H_2btec: benzene-1,2,4,5-tetracarboxylic acid was investigated by adsorbing Pb(II) ions in an aqueous solution, separating the adsorbent using centrifugation, and finally measuring the residual Pb(II) ions using the ICP-AES method.

Keywords: metal-organic framework; green synthesis; heavy metal; adsorption

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1. Introduction

With developing industrial efforts, decreasing clean water, and increasing water pollution, toxic pollution agents have become an essential problem facing human beings. Wastewaters now contain inorganic chemicals, such as heavy metals, which easily pollute the environment. Metals, including lead (Pb), arsenic (As), mercury (Hg), chromium (Cr), nickel (Ni), barium (Ba), cadmium (Cd), cobalt (Co), selenium (Se), and vanadium (V) are poisonous even in ppb (parts per billion). These toxic elements enter food and water, and even items such as toys; they can damage kidneys, the brain, nerves, and the digestive system. The concentration of lead (Pb^{2+}) in water must not surpass ppb in drinking water. Based on experiments using reticulating metal ions and organic carboxylates as linkers, it has been observed that these methods extended them and allowed for the design of structures to provide increased absorption. In this regard, a metal-organic framework (MOF) is attractive due to its exceptional high porosity. Regarding absorption, heavy metals are important, but green synthesis is also valuable. For every material, synthesized H_2O was used as a solvent, and the green synthesis method was used. The application of such green-based adsorbents could decrease heavy metal ion levels in wastewater [1,2].

2. Experimental Method

2.1. Synthesis of Experimental $[Ca(H_2btec)\cdot H_2O]_n$

In total, 1 mol (0.255 g) of benzene-1,2,4,5-tetracarboxylic acid (H_2btec) was dissolved in 20 cc water, then 10 cc ethanol was added and stirred for 2 min at room temperature until absolutely dissolved. Then, 2 mol (0.47 g) $Ca(NO_3)_2$ was dissolved in 10 cc water, and these two solutions were mixed while stirred at 100 °C, 600 rpm for 2 h, and the resulting solution was cooled to room temperature. The precipitated white powder was dried at room temperature for one day [3].

2.2. Pb(II) Ions Adsorption

In this case, the effect of different parameters, such as the effect of Pb(II) initial concentration on the absorbance mass and contact time, were studied. For the isotherm adsorption survey, all the experiments were conducted at room temperature by adding 10 mg of $[Ca(H_2btec)\cdot H_2O]_n$ to 30 mL of Pb(II) solution with an initial concentration of 12, 25, 50, and 100 mg L^{-1}. Afterward, the solution was shaken for 15 min at 100 rpm.

The Pb(II) capacity is an important factor that appoints the adsorption capacity for eliminating specific amounts of contaminants. The following Equations (1) and (2) state the contaminant elimination percentage.

$$\%R = \frac{(c_0 - c_e)}{c_0} \times 100 \quad (1)$$

$$q_t = \frac{(c_O - c_v)v}{m} \quad (2)$$

In which C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial concentration and equivalent concentration of contaminants, respectively. V (mL) is introduced as solution volume, m (g) as adsorbent mass, and q_e (mg/g) as surface equivalent adsorption capacity.

2.3. Results and Discussion

2.3.1. XRD Pattern

Figure 1 shows the XRD pattern of $[Ca(H_2btec)\cdot H_2O]_n$ and exhibits a sharp and highly intense peak at 2θ 26.5°.

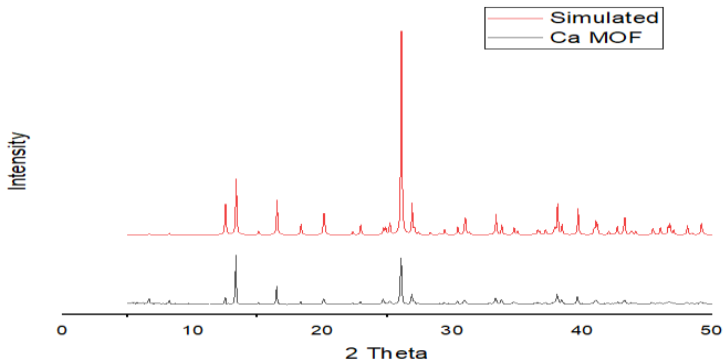

Figure 1. The XRD pattern of $[Ca(H_2btec)\cdot H_2O]_n$.

2.3.2. FTIR Spectrum

The FTIR spectrum of of $[Ca(H_2btec)\cdot H_2O]_n$ was shown in Figure 2. The bands at 3500 cm^{-1} and 3650 cm^{-1} are attributed, respectively, to carboxylic groups and water molecules. The band at 900–690 cm^{-1} is attributed to the aromatic ring of the linker.

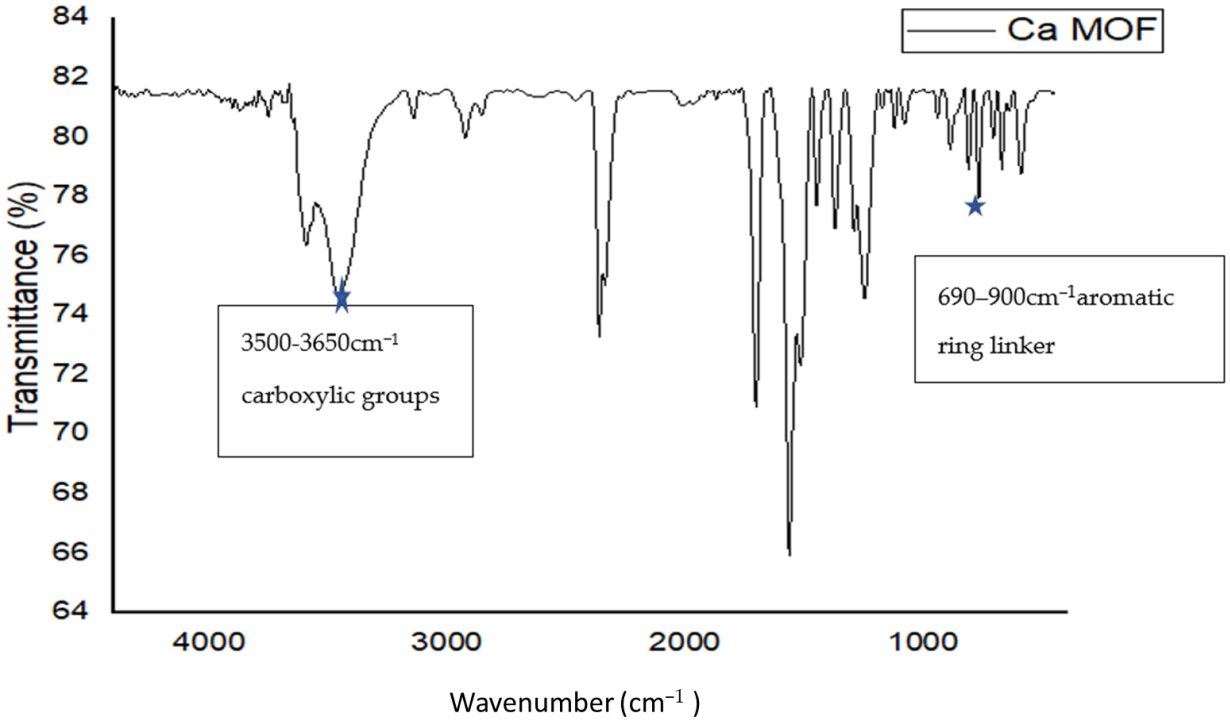

Figure 2. FTIR spectrum of $[Ca(H_2btec)\cdot H_2O]_n$.

2.3.3. Scanning Electron Microscopy

The result shown in Figure 3 illustrates the rod shapes of the MOF particles, with an average size of 1–7 µm.

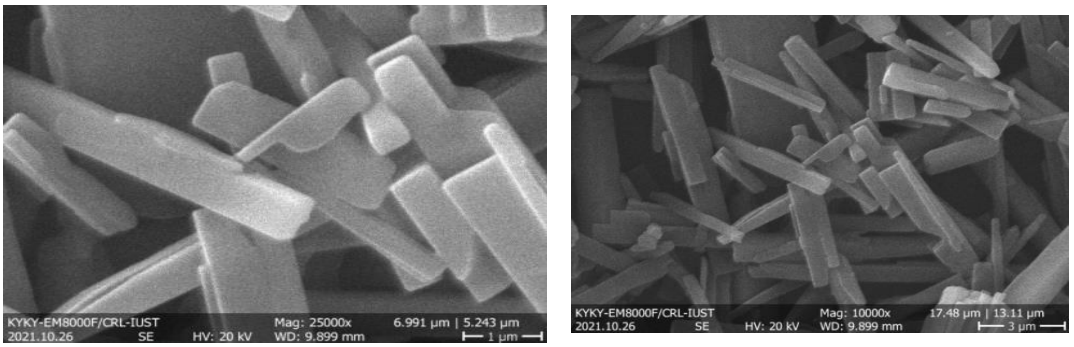

Figure 3. The SEM images of $[Ca(H_2btec)\cdot H_2O]_n$.

2.3.4. Effect of pH and Time on Adsorption

The amount of Pb(II) adsorbed onto $[Ca(H_2btec)\cdot H_2O]_n$ is a function of time and pH. As shown in Figure 4, the best pH is 5, in which more than 95% adsorption occurred. Moreover, Pb(II) adsorption is increased to 96% mg g^{-1} at 15 min, shown in Figure 5 as the highest adsorption and then it remains constant till 35 min.

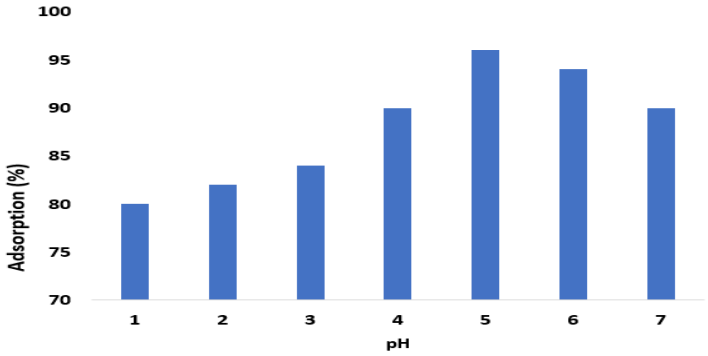

Figure 4. The effect of pH on lead absorption by $[Ca(H_2btec)\cdot H_2O]_n$.

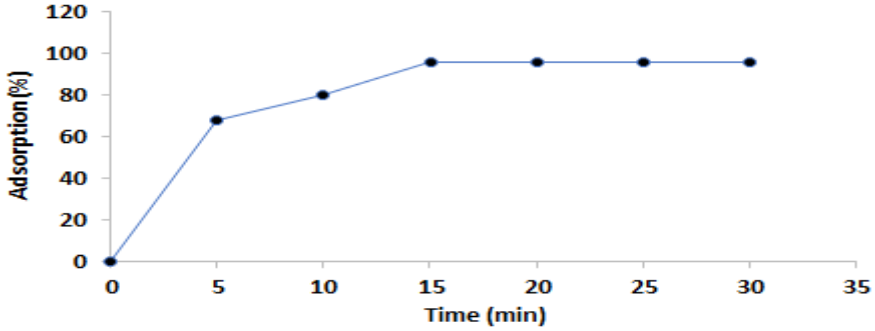

Figure 5. The effect of time on the amount of lead absorption by the $[Ca(H_2btec)\cdot H_2O]_n$.

2.3.5. Adsorption of Metallic Ions

On examining toxic metallic ions, including lead, copper, cadmium, chrome, and barium, we found out that the title MOF can adsorb the former most effectively. This can be seen in Figure 6, in which Pb(II) ions are nearly 100% adsorbed, performing much better than the others.

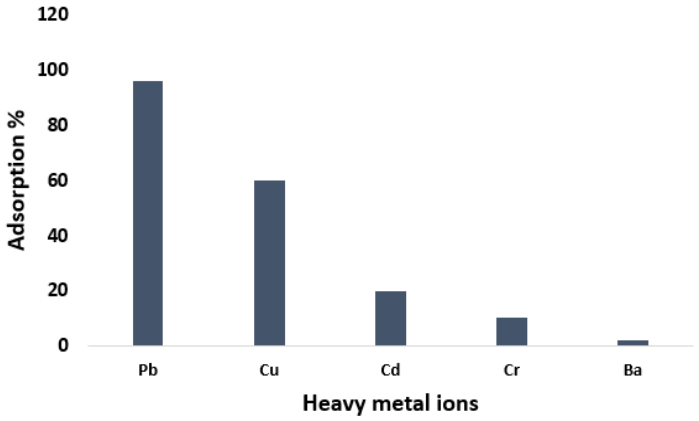

Figure 6. Comparative adsorption of various toxic ions.

2.3.6. Desorption after Adsorption

After the adsorption of Pb(II), we tried to desorb it from the adsorbent to examine whether the structure of MOF remained or not. Primarily, we searched for lead ions, and, as shown in Figure 7, the Energy-Dispersive X-ray Spectroscopy (EDX). methods results illustrate the presence of the ions in the MOF after adsorption. Afterward, we desorb the ions by removing them from the MOF in D.I. water by washing them in RT three times, then separating and drying the MOF. The XRD pattern of the empty MOF shown in Figure 8 illustrates some peaks similar to those of the initial MOF. This reveals that the MOF's structure has not been changed after the adsorption and desorption of lead ions.

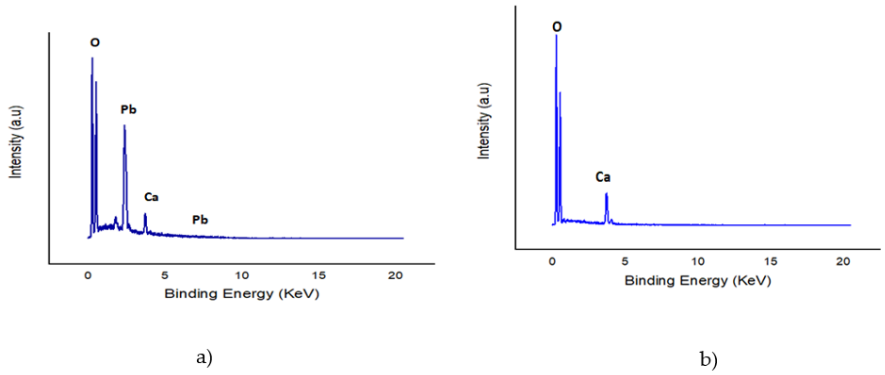

Figure 7. The EDX results (**a**) before and (**b**) after adsorption of Pb(II).

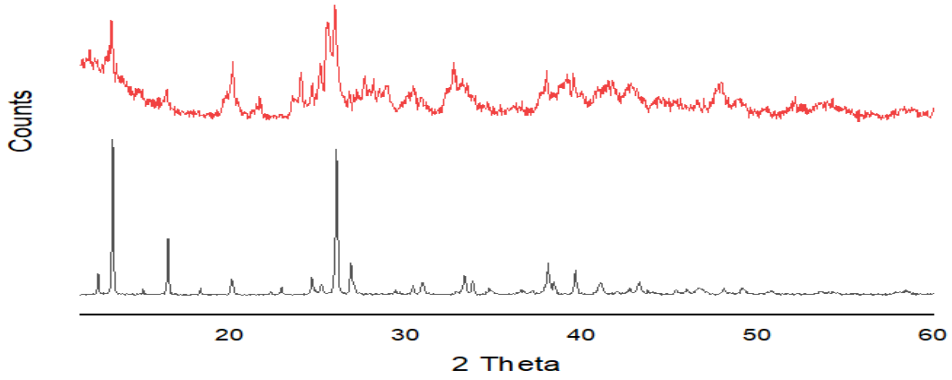

Figure 8. The XRD pattern of $[Ca(H_2btec)H_2O]_n$ before adsorption (black, bottom line) and its XRD pattern after three times of Pb(II) adsorption and desorption (red, top line).

3. Conclusions

In this work, $[Ca(H_2btec)\cdot H_2O]_n$ has been investigated for the absorption of heavy metals, and it has successfully absorbed about 96% of the Pb(II) in water after 15 min. It should be considered that the adsorbent has been synthesized using an environmentally friendly approach, and the aim was to absorb a pollutant that is very harmful to the environment. Therefore, this can be further researched using green chemistry. Finally, we found out that the MOF's structure remained after three times washes in an aqueous solution.

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